

PATENT

50293

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :
Jorge Ancheyta Juarez et al. : Art Unit 1797
Serial No.: 10/563,577 : Examiner: B. McCaig
Filed: January 6, 2006 :
For: PROCESS FOR THE CATALYTIC :
HYDROTREATMENT OF HEAVY :
HYDROCARBONS OF PETROLEUM :

SUBMISSION OF EXECUTED DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Supplementing the Amendment filed October 1, 2009 with an approved, but unexecuted Declaration Under 37 C.F.R. § 1.132 of Dr. Jorge Ancheyta-Juárez, Applicants are submitting herewith the executed declaration.

It is believed that the application is in condition for allowance. Such action is earnestly solicited.

Respectfully submitted,



David S. Abrams
Reg. No. 22,576

Roylance, Abrams, Berdo & Goodman, L.L.P.
1300 19th Street, N.W., Suite 600
Washington, D.C. 20036
(202) 659-9076

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :
Jorge Ancheyta-Juarez et al. : Art Unit: 1797
Serial No.: 10/563,577 : Examiner: B. McCaig
Filed: June 21, 2006 :
For: PROCESS FOR THE CATALYTIC :
HYDROTREATMENT OF HEAVY :
HYDROCARBONS OF PETROLEUM :

DECLARATION UNDER 37 C.F.R. § 1.132

I, Jorge Ancheyta-Juárez, hereby declare:

1. I received a split PhD degree in Chemical Engineering from Metropolitan Autonomous University (Mexico) and Imperial College London (UK) in 1998. I have been employed by “Instituto Mexicano del Petroleo” since 1989, and have worked since that time in the development of catalysts and processes for petroleum refining. At present I am R&D Project Leader and much of my research since has been devoted to the development of catalysts and processes for upgrading of petroleum.

2. I consider myself an expert in the field of upgrading of heavy oils. Part of my research work in this topic has been summarized recently in the books: “Hydroprocessing of Heavy Oils and Residua” by J. Ancheyta and J. G. Speight, Taylor and Francis Group, Boca Raton (2008), and “Asphaltenes: Chemical Transformations during Hydroprocessing of Heavy Oils” by J. Ancheyta, F. Trejo, and M. S. Rana, Taylor and Francis Group, Boca Raton (2009).

3. I am a co-inventor of the process described and claimed in the above-identified U.S. patent application.

4. I have reviewed and am familiar with U.S. Patent No. 4,657,664 to Evans et al entitled "Process for Demetallization and Desulfurization of Heavy Hydrocarbons" ("Evans et al"). In my opinion Evans et al. do not disclose nor render obvious our invention. While Evans et al. disclose broad temperature and pressure ranges, Evans et al. teach utilization of higher temperatures rather than lower pressures to achieve high conversion and removal of impurities, such as sulfur, asphaltenes and metals, and do not teach or suggest to one of ordinary skill in the art that the use of lower pressures can also achieve high conversion and removal of such impurities. Moreover, the sediment formation in the process of our invention is much lower than the commercially operable limit (0.8 wt%), whereas the sediment formation in Evans' process is very close or even higher than the limit value (0.63 to 1.18 wt%, in Table IV of Evans et al).

5. The following tests demonstrate that the use of a lower operating pressure can achieve comparable conversion and removal of impurities, such as sulfur, asphaltenes and metals from heavy hydrocarbons, such as vacuum residues. Using higher pressure does not have great advantage in respect to removal of impurities, such as sulfur, asphaltenes and metals from heavy hydrocarbons, such as vacuum residues.

In Test A, the hydrotreatment of a vacuum residue having the properties:

Properties	ASTM Method	Values
API Gravity	D-287	1.87
Total sulfur, weight%	D-4294	5.07
Total nitrogen, wppm	D-4629	6,200
Ramsbottom carbon, weight%	D-524	25.41
Asphaltenes, weight%	D-3279	25.46
Metals, wppm		
Ni+V		777.9
Sediments and sludge, weight%	D4870	0.0
Fraction IBP-538°C+, volume%		0.0

was conducted in a catalytic ebullated-bed reactor using the Ni-Mo-Titania on gamma alumina catalyst (Table 3 of our Application) under the following operating conditions, including a pressure of 100 kg/cm²:

Operating conditions

<u>Temperature, °C</u>	400
Pressure, kg/cm ²	100
LHSV, h ⁻¹	0.25
H ₂ /HC ratio, nl/l	2,671
Purity of hydrogen, mole%	100

The hydrotreated vacuum residue had the following properties and composition:

Properties	ASTM		Hydrotreated residue
	Method		
API Gravity	D-287	21.19	
Total sulfur, weight%	D-4294	0.714	
Total nitrogen, wppm	D-4629	3,800	
Asphaltenes, weight%	D-3279	3.67	
Metals, wppm			
Ni+V		47	
Sediments and sludge, weight%	D-8470	1.38	
Conversion, volume%		75.2	
Composition, volume%			
Fraction IBP-170°C		6.5	
Fraction 170-360°C		36.4	
Fraction 360-538°C		32.3	
Fraction 538°C+		24.8	
Fraction IBP-538°C+		75.2	

6. For comparative purposes, a second test, Test B, was conducted in which a vacuum residue having the properties:

Properties	ASTM Method	Values
API Gravity	D-287	3.73
Total sulfur, weight%	D-4294	4.507
Total nitrogen, wppm	D-4629	6,100
Conradson carbon, weight%	D-524	22.59
Asphaltenes, weight%	D-3279	17.75
Metals, wppm		
Ni+V		502.6
Sediments and sludge, weight%	D4870	0.0
Fraction IBP-538°C, volume%		0.0

was subjected to hydrotreatment also using the Ni-Mo-Titania on gamma alumina catalyst of Test A in an ebullated bed reactor but at a higher pressure of 185 kg/cm² as follows:

Operating conditions

<u>Temperature, °C</u>	420
Pressure, kg/cm ²	185
LHSV, h ⁻¹	0.30
H ₂ /HC ratio, nl/l	1,335
Purity of hydrogen, mole%	100

The hydrotreated vacuum residue has the following properties:

Properties	ASTM	Hydrotreated residue
	Method	
API Gravity	D-287	18.0
Total sulfur, weight%	D-4294	2.12
Total nitrogen, wppm	D-4629	3,760
Asphaltenes, weight%	D-3279	5.58
Metals, wppm		
Ni+V		68.4
Sediments and sludge, weight%	D-8470	1.0
Conversion, volume%		71.9
Composition, Volume%		
Fraction IBP-170°C		12.9
Fraction 170-360°C		26.0
Fraction 360-538°C		33.0
Fraction 538°C+		28.1
Fraction IBP-538°C+		71.9

7. Based upon the foregoing test results, the conversion removal of sulfur, nitrogen, asphaltene and metals in Test A using an operating pressure of 100 kg/cm² is 85.92%, 38.70%, 85.58% and 93.96%, respectively. However, in Test B when a higher pressure of 185 kg/cm² is used, the removal of sulfur, nitrogen, asphaltene and metals is 52.96%, 39.34%, 68.56% and 86.39 %, respectively. Although it is not totally desirable to compare two tests with slight differences in the feed properties, it is roughly demonstrated that the use of higher operating conditions like pressure and temperature in test B does not produce very promising results. The

test results essentially show that the conversion removal of sulfur, nitrogen, asphaltene and metals in Test A using an operating pressure of 100 kg/cm² are comparable or even better than those obtained in Test B when a higher pressure of 185 kg/cm² is used. Apart from the use of a slightly different feed, the test results confirm that using higher pressure (Evans et al.) does not produce great advantages as compared with lower pressure (our invention). Therefore, the lower pressure could be used to upgrade heavy crude oils or residue instead of using very high pressure and high temperature which is also very costly process.

8. Tests A and B, therefore, demonstrate that the use of a lower operating pressure achieved improved sulfur (85.92% vs. 52.96%), asphaltene (85.58% vs. 68.56%) and metal removal (93.96%, vs. 86.39 %). Also the API gravity (21.9 vs. 18) and total volumetric conversion (75.2% vs. 71.9%) are also higher using the lower operating pressure of Test A. The combination of high pressure and temperature, i.e. high reaction severity, is oriented the reaction towards the production of other light components, e.g. light gases, thus changing the selectivity and extent of the other reactions, e.g. impurities removals. These results are very significant, since using lower process pressure presents fewer, problems e.g. sediment formation, and is more cost effective than using higher process pressures or higher temperatures.

9. We have also made a brief comparison of the catalysts used in our invention and that used by Evans et al. as given below:

Our Catalysts (Table 3 of our Application)			Evans et al., Table 1		
	HDM	HDS		Catalyst A (HDM)	Catalyst B (HDS)
Surface area (m ² /g)	175	248	Surface area (m ² /g)	182	320
Pore Volume, (cm ³ /g)	0.56	0.51	Pore Volume in pores greater than 1,200 Å diameter, (cm ³ /g)	0.41	0.16
Mean pore diameter, (Å)	127	91	Mean pore diameter, (Å)	200	88
Molybdenum, wt%	10.66	12.89	MoO ₃ , wt%	4.2	14.6
Nickel (NiO), wt%	2.88 (3.6)	-			
Cobalt (CoO), wt%	-	2.5 (3.2)	CoO, wt%	-	3.6
Sodium, wt%	412	-	SiO ₂ , wt%	3.6	-
Titania, wt%	3.73	3.20	Al ₂ O ₃ , wt%	balance	balance

Our HDM and HDS catalysts are NiMo and CoMo supported on gamma alumina, respectively. Both catalysts also contain more than three weight percentage of titania. However, catalyst A of Evans et al. does not contain promoter (nickel or cobalt) whereas catalyst B contains 3.6 wt % CoO in Evans et al. Catalysts A and B are supported on SiO₂-Al₂O₃ and alumina, respectively. The Evans et al catalysts do not contain TiO₂. It is very apparent that the functionalities of our catalysts are different than those of Evans et al. due to the presence of

different types of promoter metal or metals. Moreover, Evans et al. employed the catalysts supported by more macroporous material than in the process of our invention. Evans et al. use supports having pore volume for pores larger than 1200 Å, of about 0.1-0.4 cm³/g (Column 8, line 31). In the process of our invention, the support has pores in the range of 500-2000 Å diameter, and a pore volume for this range of about 0.34 cm³/g (0.56 cm³/g x 6.09 vol.% = 0.34 cm³/g from Table 3 of our Application). All these differences also contribute to the better results of the process described in our Application as compared with those reported by Evans et al.

10. In my opinion, the results we achieve as indicated from the foregoing tests, including low sediment formation, while using lower temperature and pressure are neither obvious nor apparent from the Evans et al. patent. The properties of the respective catalysts are different. We use NiMoTiO₂ and CoMoTiO₂ each supported on gamma alumina, which catalysts are not disclosed by Evans et al. By using the catalysts of our invention with lower temperatures and pressures, we are able to provide the advantages of the lower operating costs and simplicity of our process.

11. I hereby declare further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Dated: Sept. 30 / 2009

